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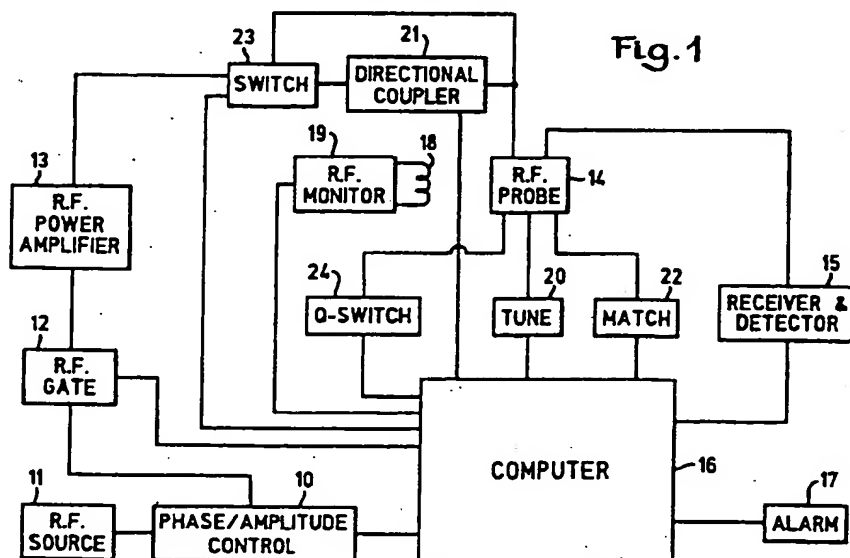(74) Agent and/or Address for Service
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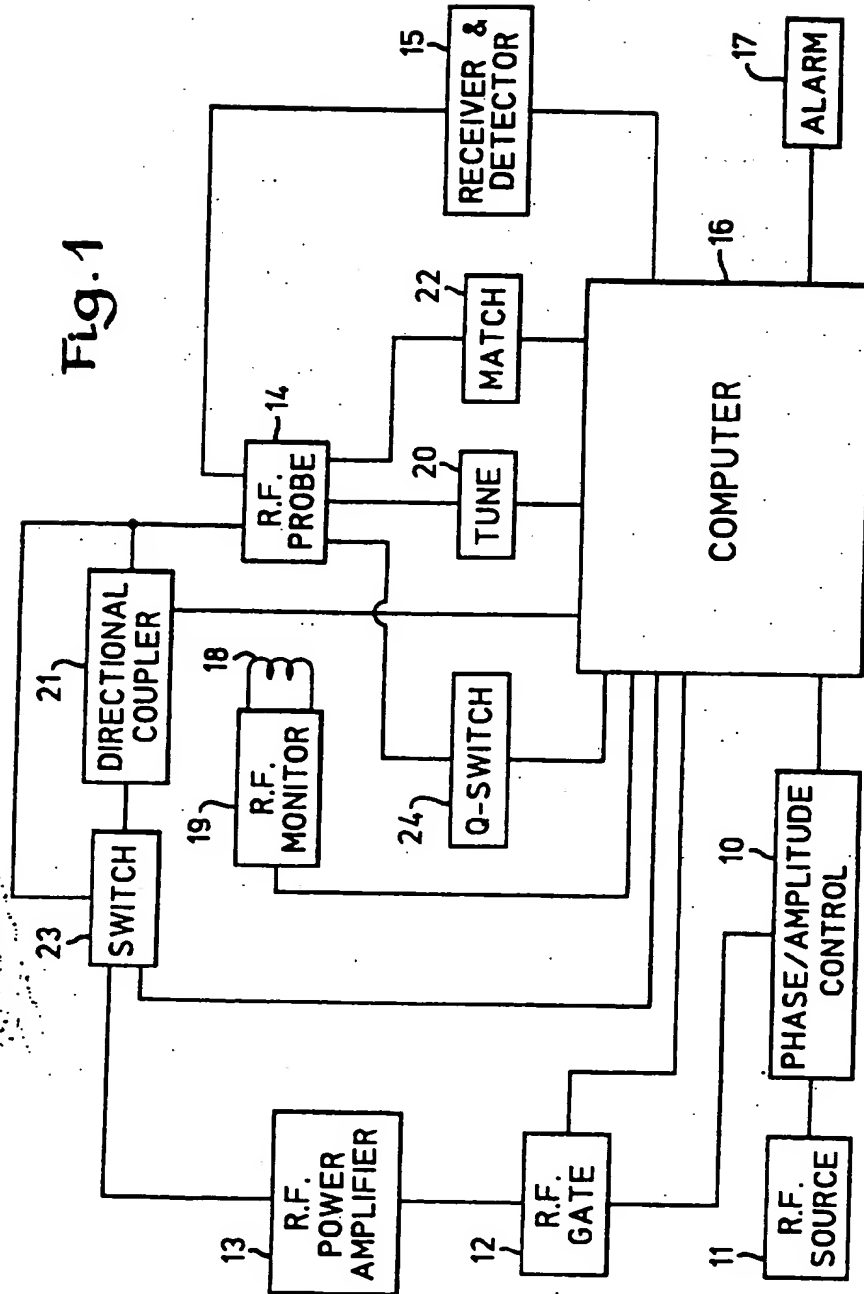100 Grays Inn Road, LONDON, WC1X 8AL,
United Kingdom

(54) Testing a sample by nuclear resonance

(57) A method of detecting the presence of a particular substance in a given sample comprises exciting nuclear resonance in the substance and detecting the response signals from the substance using a probe 14, and adjusting the probe in dependence on the character of the sample. The adjustment may be by means of altering the probe impedance, returning the probe or adjusting its Q-value. Further methods of avoiding interfering signals by blanking detection for a short time after excitation and using two different types of excitation are disclosed. The result of the sample detection can be used to adjust the probe.
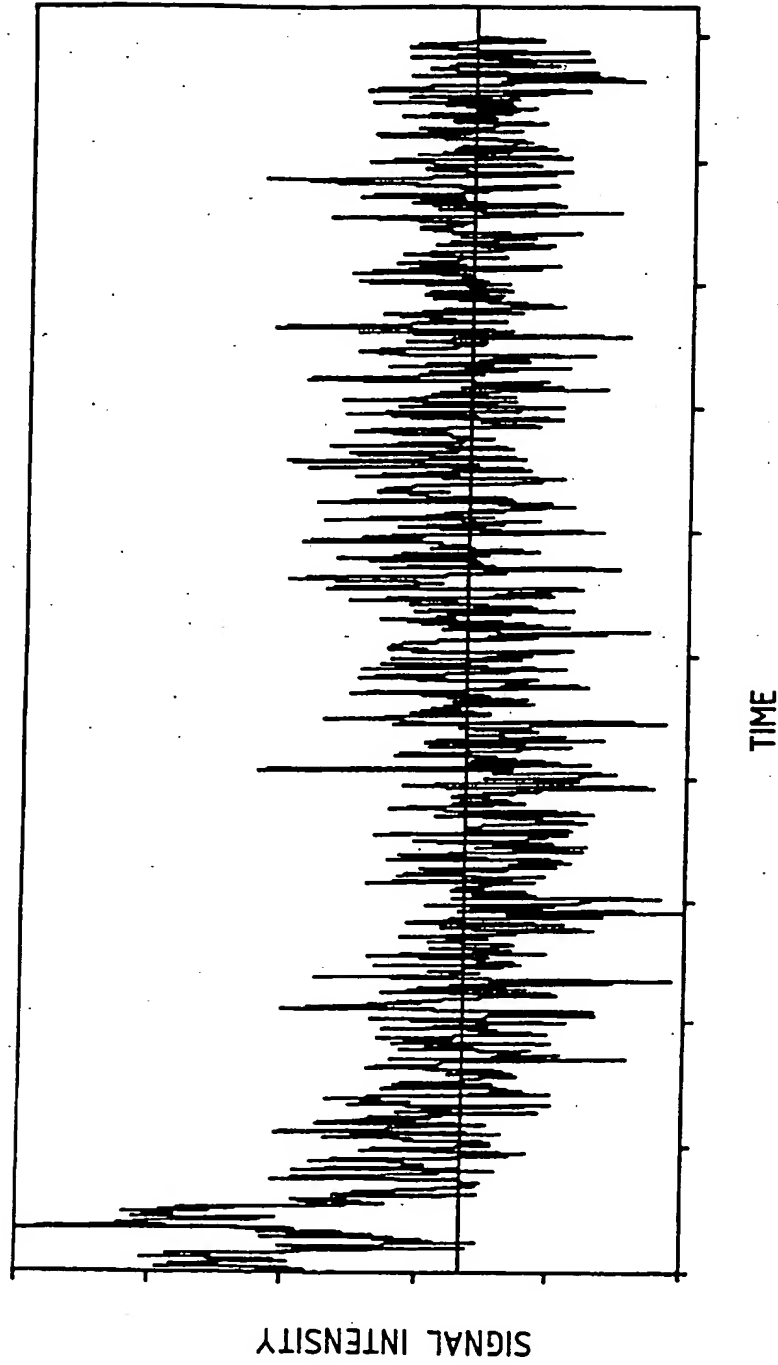

Fig. 1

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Fig.1

Fig. 2

TIME

SIGNAL INTENSITY

FREQUENCY

SIGNAL INTENSITY

Fig. 3

SIGNAL INTENSITY

TIME

Fig.4

Fig.5

FREQUENCY

SIGNAL INTENSITY

FREQUENCY

SIGNAL INTENSITY

Fig.6

Fig.7

SIGNAL INTENSITY

FREQUENCY

Fig. 8

TIME

SIGNAL INTENSITY

Fig.9

Fig. 10

FREQUENCY

SIGNAL INTENSITY
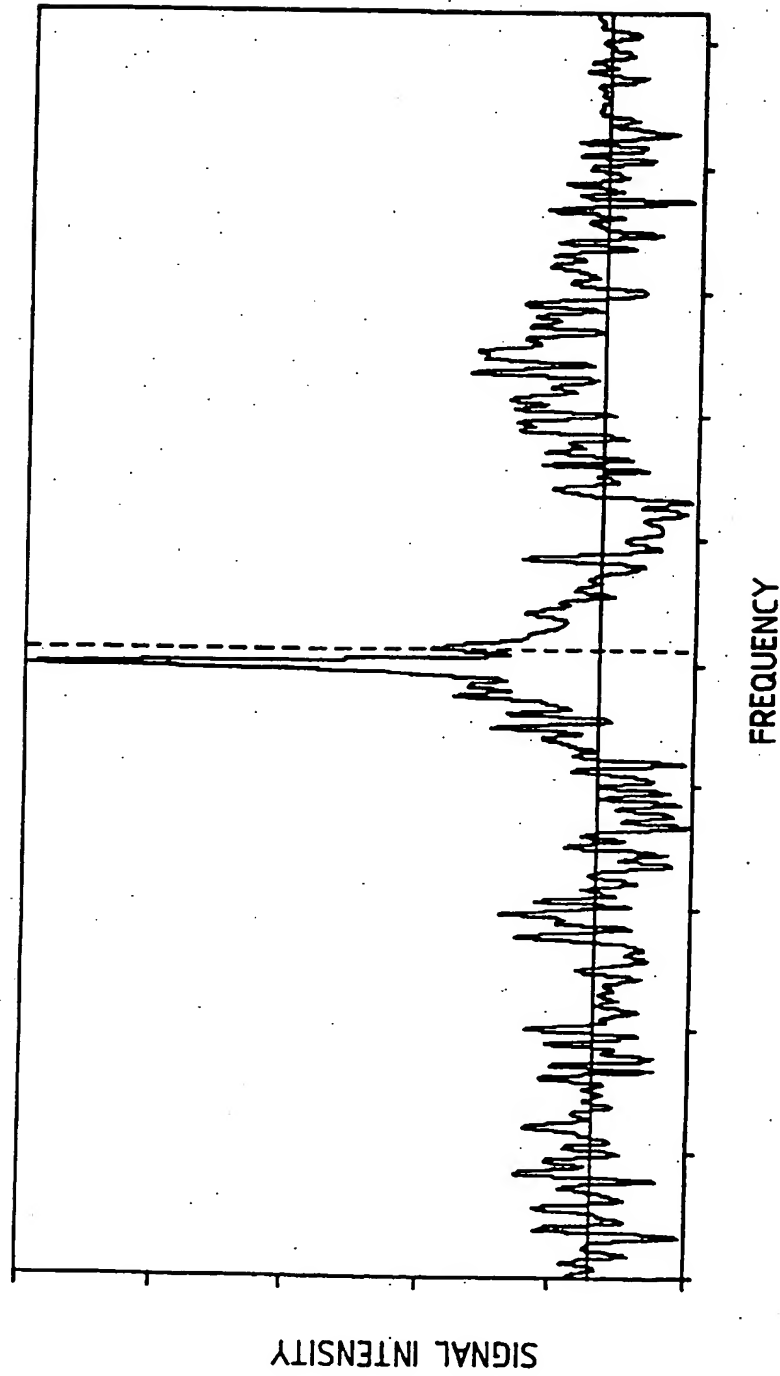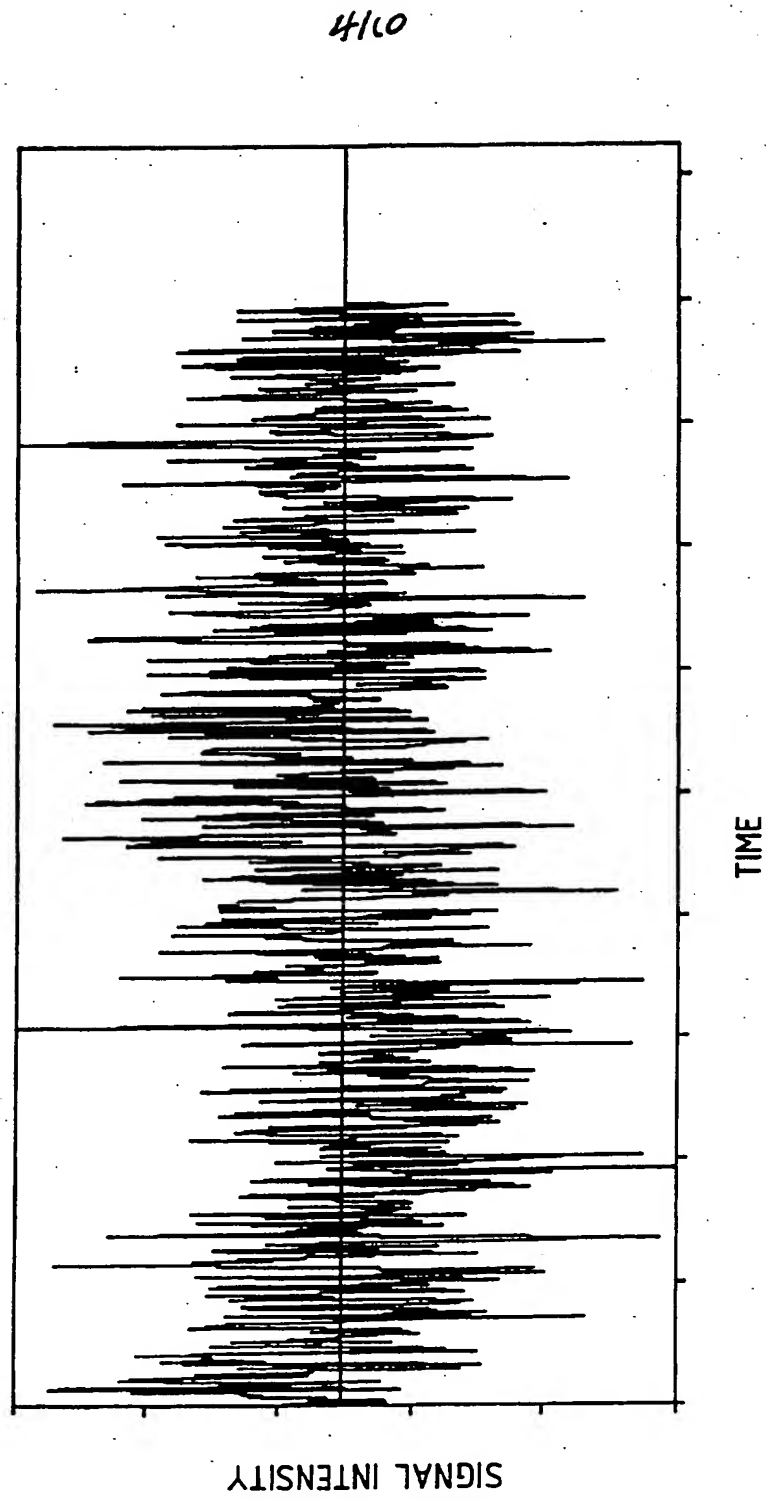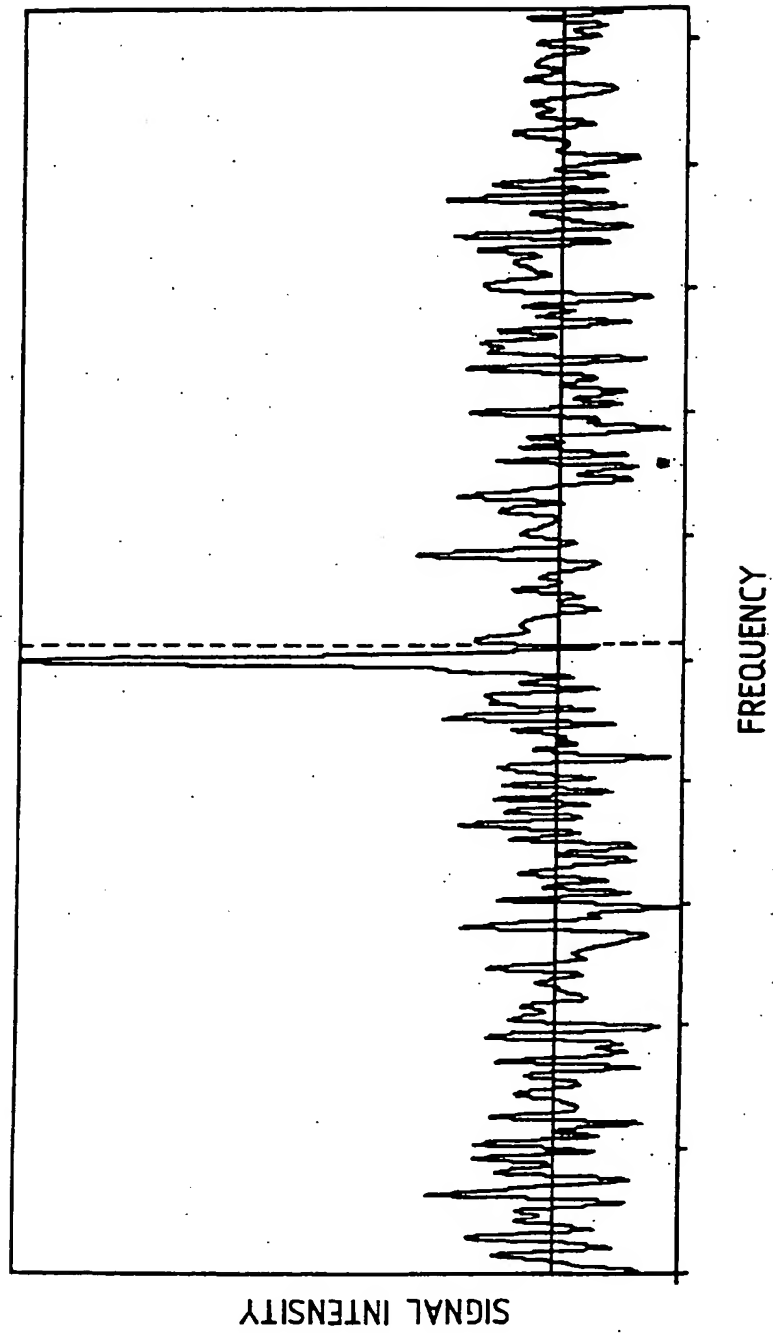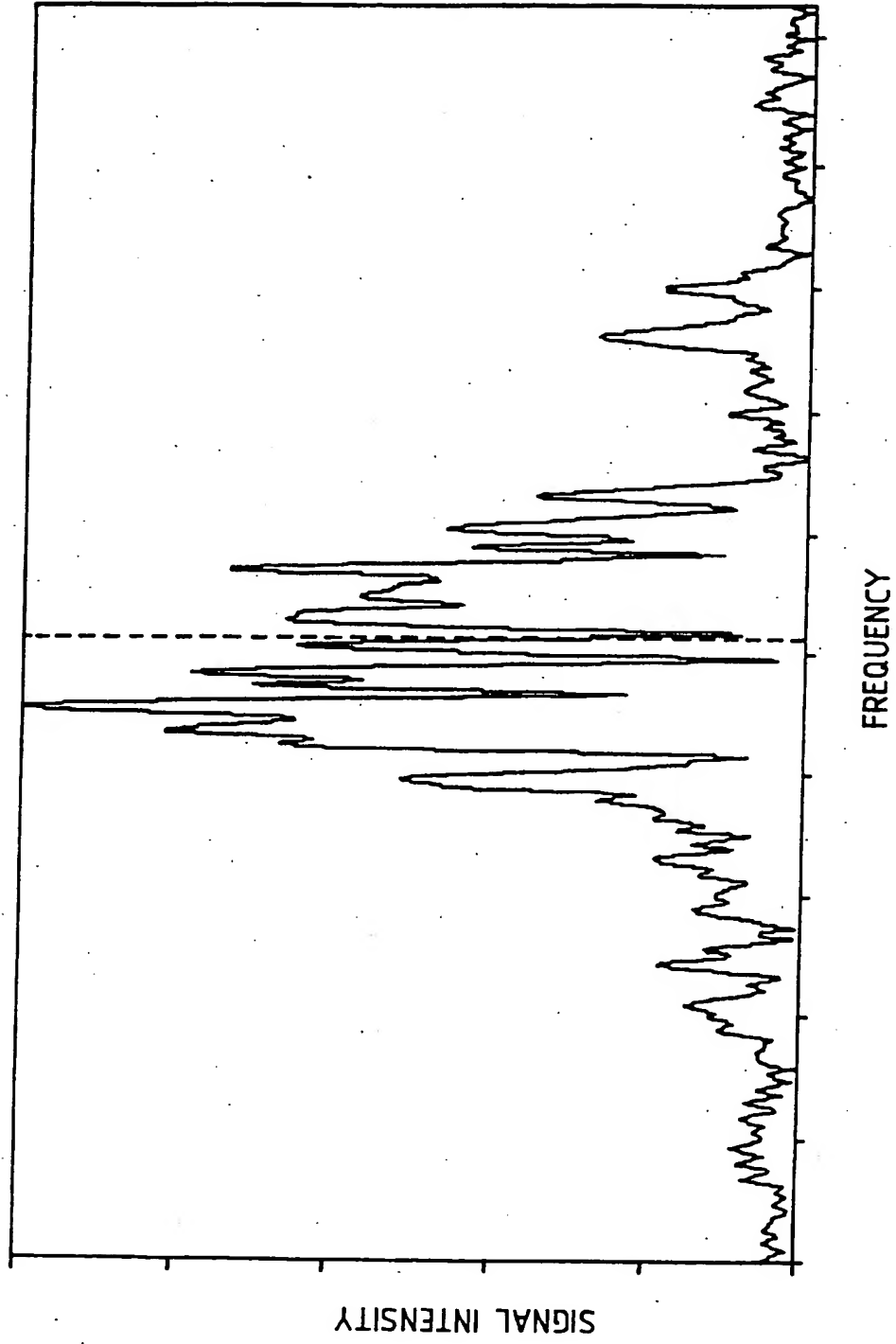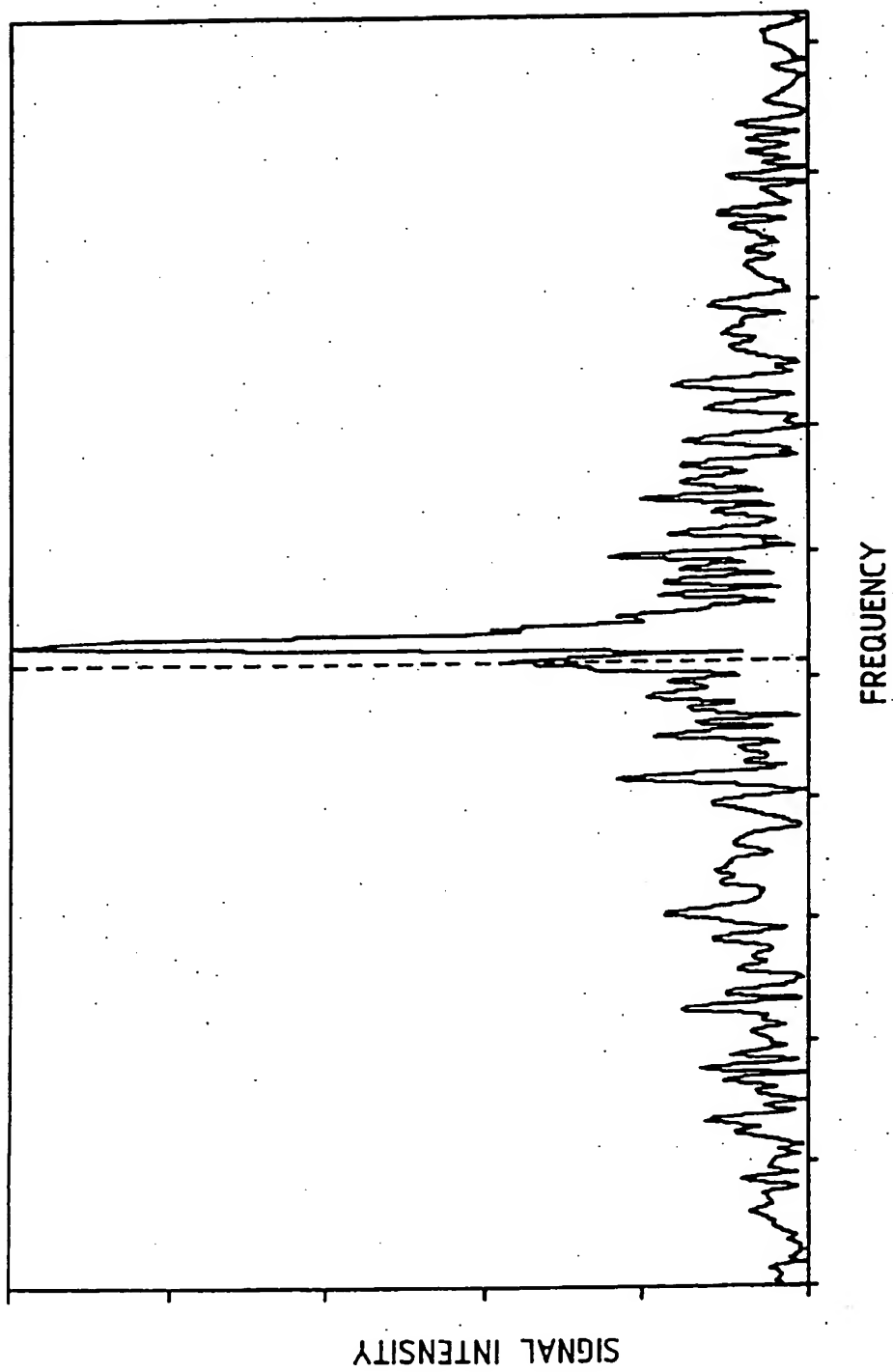
5   METHOD OF AND APPARATUS FOR TESTING A SAMPLE

The present invention relates to a method of testing a
sample, and to apparatus for testing the sample. It
relates especially to Nuclear Quadrupole Resonance (NQR)
testing a sample containing or suspected of containing
10 nuclei of integral or half-integral spin quantum number (I
> ½).

NQR testing is used for detecting the presence or
disposition of specific substances. It depends on the
15 energy levels of quadrupolar nuclei, which have a spin
quantum number I greater than ½, of which ^{14}N is an example
(I = 1). ^{14}N nuclei are present in a wide range of
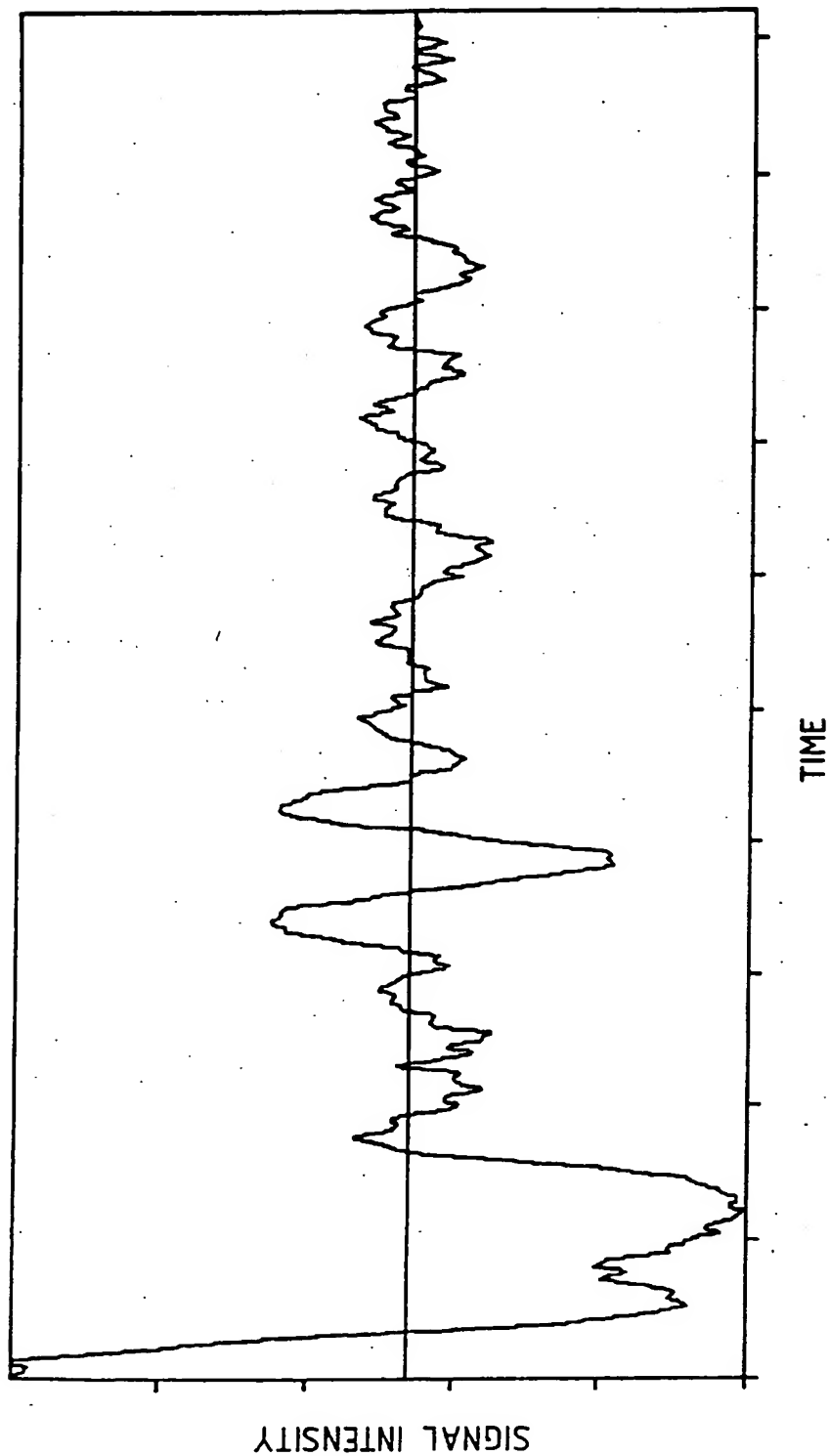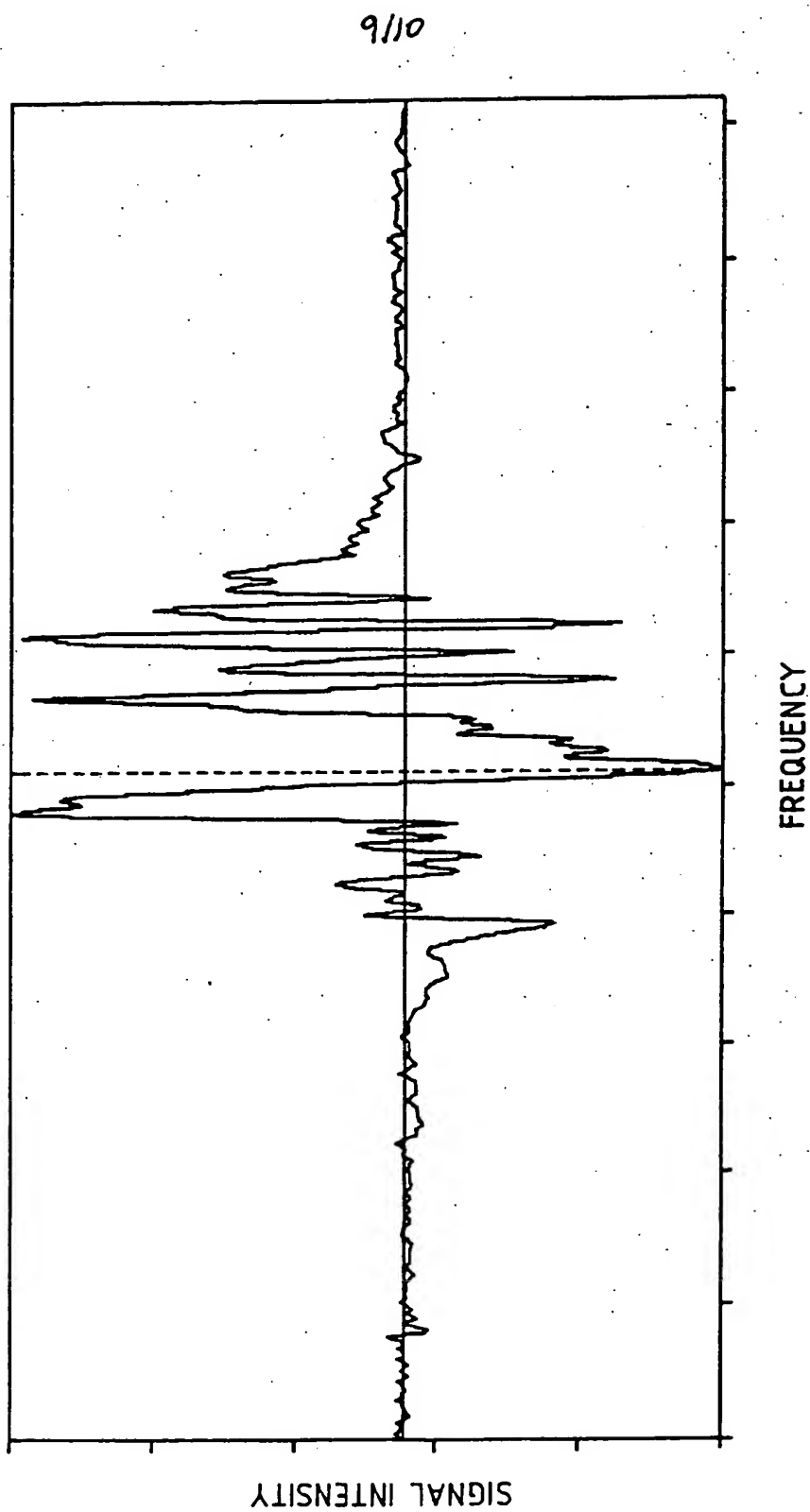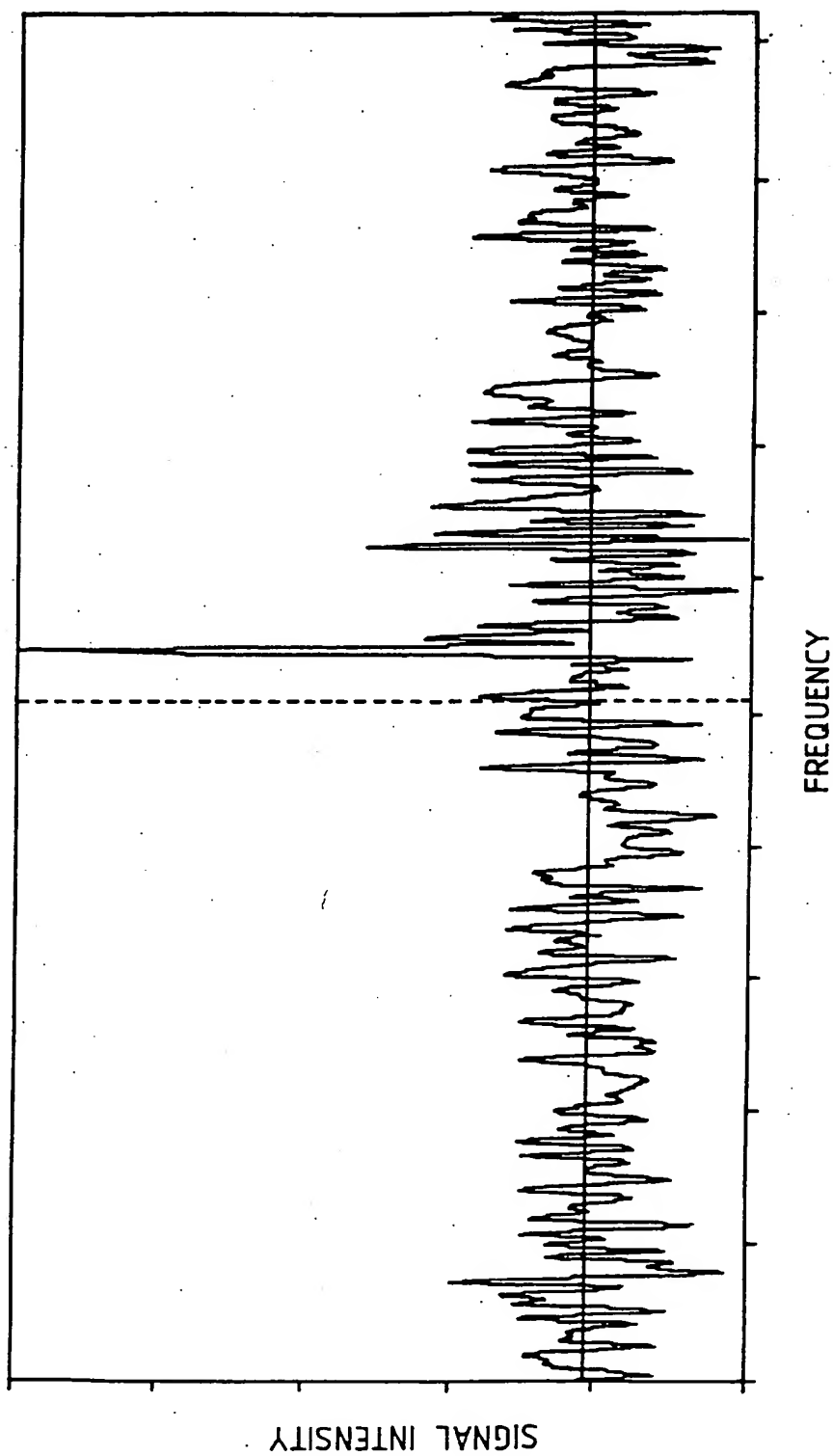substances, including animal tissue, bone, food stuffs,
explosives and drugs. One particular use of the technique
20 of the present invention is in the detection of the
presence of substances such as explosives or drugs. The
detection may be of baggage at airports, or of explosives
or drugs concealed on the person or buried underground.

25 In the molecular environment of compounds in crystals, the
nature and disposition of the electrons and other atomic
nuclei close to the nucleus of interest produce an electric
field gradient at the latter which interacts with its
electric quadrupole moment to generate a set of energy
30 levels, the transition frequencies between which are
characteristic for a given substance. The presence of this
frequency or frequencies not only indicates which nuclei
are present, but also their chemical environment, thus
indicating specific substances or types of substances in
35 any tested sample.

In conventional NQR testing a sample is placed within or
near to a radio-frequency (r.f.) coil and is irradiated
with pulses or sequences of pulses of electro-magnetic
40 radiation having a frequency which is at or very close to
a resonance frequency of the quadrupolar nuclei in a

substance which is to be detected.   If the substance is present, the irradiant energy will generate a precessing magnetisation which can induce voltage signals in a coil surrounding the sample at the resonance frequency or

5 frequencies and which can hence be detected as a free induction decay (f.i.d.) during a decay period after each pulse or as an echo after two or more pulses.   These signals decay at a rate which depends on the time constants T_2^* for the f.i.d., T_2 and T_{2e} for the echo amplitude as a

10 function of pulse separation, and T_1 for the recovery of the original signal after the conclusion of the pulse or pulse sequence.

In conventional NQR testing, either a substantial part of

15 the f.i.d. is measured after each pulse or the responses are measured as echoes in the relatively short sampling periods between or following a succession of two or more pulses.   Usually the results from a number of test pulses or test sequences are accumulated to improve the signal-to-

20 noise ratio.   Various schemes of pulse sequences have been used.

The present invention arises, in one aspect, from the surprising discovery that, in the detection of the presence

25 of a particular substance in a given sample using nuclear resonance techniques, interfering signals may arise from the sample which may swamp the genuine nuclear resonance signals.   This is particularly so in circumstances where the amount of the particular substance is much less than

30 the amount of the remainder of the sample, and the interfering signals arise from the remainder of the sample. Such circumstances, it has now been discovered, occur commonly.   For example, small amounts (maybe only a few tens of grams) of narcotics are frequently concealed within

35 bulky pieces of airport baggage.   Many common household items carried in baggage, it has been found, are likely to give rise to interfering signals.

The problem of one kind of interference when testing a particular substance is known from a book entitled "Experimental Pulse NMR", by Fukushima, E. et al., Addison-Wesley Publishing Company, Inc., pp. 466ff. The interference takes the form of spurious ringing caused by piezo-electric resonance of the substance. However this problem is not disclosed in the context of detecting the presence of the substance within a given sample.

It is known from this book to solve this particular interference problem by using an electrostatic shield (Faraday shield) between the sample and the NMR probe (usually a coil) to reduce the interference. However, such a shield can be bulky and unwieldy. Furthermore, it has been discovered pursuant to the present invention that, particularly with NQR testing, there may be different types of interference other than that caused by piezo-electric resonance, and that the Faraday shield may not successfully reduce all these types of interference.

Also, it is known from a book by Cady, E.B. entitled "Clinical Magnetic Resonance Spectroscopy", Plenum Press (1990) (see pages 160ff.) in the field of Nuclear Magnetic Resonance Imaging to adjust the NMR probe according to the nature (for instance, size) of the body being imaged. This adjustment is not to take account of interfering signals from the body; rather, the body is actually the "substance" under test, and the adjustment is to ensure appropriate "matching" of the probe and the body. A similar technique is known from European Patent No. 0 180 121.

Such adjustment has not hitherto been contemplated for nuclear resonance techniques involving the detection of the presence of a particular substance in a given sample, partly, perhaps, because the amount of the substance under test is generally so small in relation to the total amount of the sample and the volume probed by the probe (that is,

the filling factor is so small), that the possibility of requiring matching between the probe and the substance/sample has never been contemplated. Typically, the filling factor might be only a fraction of one percent.

5

According to a first aspect of the present invention, there is provided a method of detecting the presence of a particular substance in a given sample comprising exciting nuclear resonance in the substance and detecting the response signals from the substance, using a probe, and adjusting the probe in dependence on the character of the sample.

It has been found pursuant to the present invention that adjustment of the probe in dependence on the character of the sample can have the advantage of reducing interference from many types of substances (other than the substance of interest) commonly found in a typical sample such as airport baggage. Hence the invention can provide more accurate and sensitive tests than if such adjustment does not take place, and can also reduce the false alarm rate.

In the present invention, there is no need to adjust the probe in dependence on the character of the particular substance at all. The filling factor of the substance would be assumed to be so small (a fraction of one percent, say, corresponding to a few tens or hundreds of grams of explosive in a suitcase) that adjustment of the probe in dependence on the character of the substance is simply not necessary.

Preferably, the probe is adjusted (or adjustable) whilst it is in operation. This feature is particularly advantageous if baggage is being checked for the presence of explosives or drugs, for instance on a conveyor at an airport. The nature of the interference from each individual item of baggage may be different, and hence the sensitivity of the

tests can be improved by adjusting the probe individually for each item of baggage.

The principles underlying this aspect of the invention are
5 as follows.   In the case of NQR testing, it has been determined pursuant to the present invention that there are two groups of materials which produce interference problems that may require adjustment of the r.f. probe usually used in NQR testing.
10

The first group includes metallic conductors which conduct electronically, such as brass, copper and aluminium. Such materials may be commonly found in many types of objects in baggage, for instance, in electronic circuitry. For this
15 group, the interference effects are caused largely by eddy currents induced by the NQR r.f. excitation. These effects may be particularly acute in the case of metallic loops such as leads or connections on printed circuit boards or on metal sheet. They cause electrical loading and thereby
20 alter the inductance of the sample coil forming part of the r.f. probe, and hence change the resonance frequency of the probe (since the probe may be considered to include a resonant circuit of which the inductance of the coil forms one part). If the quality factor (Q) of the coil lies
25 within the usual range (20 to 60, for example), so that the probe has a relatively narrow bandwidth, then the resonance frequency of the probe may be shifted so far that the sensitivity for NQR detection is significantly reduced. Further, a change in the inductance of the sample coil may
30 also adversely affect the matching between the probe and the r.f. transmitter. Also, the Q factor itself may be adversely affected by a change in the inductance of the sample coil, so that the sensitivity of detection is adversely affected. It will be understood that $Q = \omega L/R$
35 (where ω is the (angular) resonance frequency of the probe, L is the inductance of the coil, and R is the series resistance of the probe) and that signal-to-noise ratio

(and hence sensitivity of detection) varies as the square root of Q.

Included in the first group as a special case are magnets
5 and magnetic materials.   Such magnets, if made of
electronic conductors, as would usually be the case, would
cause interference effects similar to those described in
the preceding paragraph.   However, they can also cause a
shift in and possibly even a splitting of the particular
10 resonance line of interest. Although the probe may require
re-tuning to take account of these additional effects, it
is not believed that this would normally be necessary.

The second group of materials includes non-metallic
15 materials which conduct ionically, such as wet sand or soil
and the electrolyte in batteries.   Like the first group of
materials, this second group also has the effect of
altering the resonance frequency and Q factor of the probe,
but this time through the mechanism of dielectric loss,
20 which causes a change in the resistance of the probe and
also causes a change in its inductance.

In putting the first aspect of the present invention into
practice, the invention suitably provides that the presence
25 (and character) of such interfering materials is detected
and then acted upon by effecting suitable adjustment of the
probe.

Detection of such materials is preferably effected by
30 measuring the back-reflected r.f. power from the sample,
for example, using a directional coupler. An increase in
back-reflected power indicates that the probe is no longer
correctly tuned and hence indicates the presence of an
interfering material.
35

Adjustment of the probe may be effected firstly by
adjusting the matching of the probe to the r.f. transmitter

(that is, by adjusting the impedance of the probe). This may be achieved, for example, by insertion of a ferrite rod into a tapped inductance in the probe circuitry, the rod being moved by a stepper motor programmed to seek the
5 position of minimum back-reflected wave as measured for instance by a directional coupler.

Secondly, the resonance frequency of the probe may be adjusted by automatically tuning the probe via a servo or
10 stepper motor on the axis of a variable capacitor in the tuning circuitry. The capacitance is varied until the r.f. field amplitude (B$_{r.f.}$) is a maximum, as monitored by a simple pick-up coil placed near the r.f. coil. The alternating voltage induced in the pick-up coil could be
15 rectified by either a diode or a quadrature detector and the resulting d.c. voltage fed to the control computer by means of an Analogue to Digital Converter, where it could be compared with a known reference voltage, the difference between the two being used to control the stepper motor.
20 The same quadrature detector and transient recorder could be used both for the main coil and the pick-up coil, which could render this technique relatively cheap.

Finally, it might be necessary to check that the Q factor
25 of the r.f. coil was unchanged, which could be done automatically in a short time by frequency sweeping the r.f. pulse in small steps, so as to measure the frequency difference $\Delta v = |v_1 - v_2|$, where v_1 and v_2 are the frequencies at which the r.f. current (as measured by a
30 pick-up coil) has dropped to 0.71 of its maximum value, and then using the well-known equation

$$Q = \frac{v}{\Delta v} = \frac{(v_1 + v_2)}{2|v_1 - v_2|}$$

35

to derive a value for Q.

If the Q has diminished significantly its value can be restored by removing damping devices such as metal paddles or series resistors deliberately fitted for this purpose. Alternatively, the NQR test instrument, once forewarned,

5 could be programmed to perform the test with more accumulations to overcome the effect of the drop in Q; since signal-to-noise ratio is proportional to $Q^\frac{1}{2}$, the number of accumulations must be increased by the factor Q_{old}/Q_{new}. Further, the r.f. power needs to be increased if

10 Q is lower in order to maintain the same flip angle.

It will be appreciated that not all of the above three adjustments may be necessary. However, if they are, they should preferably be carried out in the order (i) Tuning,

15 (ii) Matching, (iii) Q factor adjustment, although other orders are possible. Further, the various adjustments may interact with one another, so that an interactive set of adjustments may need to be carried out. The three adjustments proposed above may take, say, between 0.1 and

20 1 second, perhaps 0.2 to 0.5 seconds.

In certain circumstances, for example, a sheet of RDX next to a metal sheet (or sandwiched between two metal sheets) of sufficient thickness, the r.f. field may be very

25 significantly compensated by eddy currents, thereby considerably reducing sensitivity. In these and other circumstances the NQR testing apparatus may be arranged to provide an alarm signal of insensitivity or of the presence of metal. Appropriate remedial action (such as increasing

30 the r.f. power and/or number of accumulations, or hand-inspection of the particular object under suspicion) can then be taken.

According to a second aspect of the present invention,

35 there is provided a method of nuclear resonance testing a sample, comprising exciting nuclear resonance in the sample, and detecting and processing the response signal

from the sample in such a way as to at least partially filter out interfering signals, not due to nuclear resonance, arising from the sample.

5   It will be understood that, in the context of the detection of the presence of a particular substance in a sample, it would usually not be the substance to be detected but the remainder of the sample which would give rise to the interfering signals.
10

By filtering interfering signals via the detecting and processing means rather than by means of a Faraday cage physically surrounding the sample, the present invention can be considerably simpler to put into practice,
15   especially in the case of baggage being tested on a conveyor belt.

It is possible to, and in certain cases of strong electric interference, it may be necessary to, use both a Faraday
20   cage and signal detection and processing techniques.

The invention is preferably performed in the absence of an applied magnetic field.

25   A further discovery pursuant to the present invention is that there are materials such as ferromagnetic materials, certain steels or nickel-plated objects (for instance, screws or key-rings) which produce a strong spurious signal immediately following the r.f. pulse which is frequency and
30   phase coherent with the pulse and which cannot therefore be reduced by repeated accumulations (unlike most other interference, which can be).   The precise cause of this type of interference has not been proven, but it is believed to emanate from ferromagnetic or like resonance
35   effects in the B_1 field of the sample coil.   It should be emphasised that this interference is not an artefact of the

particular detection apparatus used, but a feature of the material itself.

Piezo-electric materials may also produce frequency and
5 phase coherent mechanical resonances which may lie in the frequency range of the NQR response. For instance, sand can produce interference at an r.f. frequency of 5 MHz.

It may be necessary to compensate for this interference by
10 adjusting the probe, as discussed above, unless the interference emanates from piezo-electric materials, which are non-conductors. Further, since the effects of the interference cannot be reduced by repeated accumulations, there is a requirement to provide suitable techniques for
15 reducing these effects. The present invention provides these techniques in two further aspects.

In a first such aspect, there is provided a method of nuclear resonance testing a sample, especially one which
20 gives rise to interfering signals, not due to nuclear resonance, comprising exciting nuclear resonance in the sample, and detecting the response signal from the sample, there being a delay of a predetermined duration between the end of the excitation and the beginning of the detection.
25
This aspect arises from the discovery pursuant to the present invention that the spurious signals constituting the interference decay rapidly after the r.f. pulse, usually within, say, 350, 500, 750 or 1000 μs of the end of
30 the r.f. pulses. Thus, provided the decay time of these signals is significantly less than the f.i.d. time (T_2*) or echo decay times (T_2, T_{2e}) of the NQR response, useful response data can be derived by delaying detection of the response signal for a predetermined duration, until all or
35 the bulk of the spurious signal has decayed. A delay of 500, 600 or 700 μs has been found empirically to be satisfactory in most circumstances. A sufficient decay for

the response signal might be to below 20, 10 or 5% of its initial peak value.

On the basis of a delay of 500, 600 or 700 µs, this aspect
5 of the invention would be particularly suited to materials exhibiting a T_2^*, T_2 or T_{2e} greater than, say, 1ms, so that the spurious signal has ample time to decay before there is a serious loss in the NQR response signal. One such material is the explosive RDX, which has one frequency with
10 a T_2^* of 1.4ms at room temperature.

Thus it will be understood that in practice there are both upper and lower bounds on the duration of the delay. The lower bound is dictated by the requirement that the
15 spurious interfering signals have sufficient time to decay to negligible or near-negligible levels. The upper bound is dictated by the requirement that the NQR response signal has not decayed so much that no useful response data can be detected.
20

The delay between the end of the excitation and the beginning of the detection could be taken to be additional to the receiver dead time, which is usually about 100 to 150 µs for the substances of widest interest, but may in
25 certain circumstances be as high as 500 µs.

In one preferred embodiment, the excitation is such as to cause a free induction decay response signal, and the delay occurs during this response signal. In another preferred
30 embodiment, the excitation is such as to cause an echo response signal, and the delay occurs between the end of the excitation (normally the refocussing pulse) and the echo response signal.

35 In a second such aspect of the present invention, there is provided a method of nuclear resonance testing a sample, comprising exciting nuclear resonance in the sample using

at least two different types of excitation, such that the
nuclear resonance can be distinguished from interfering
signals, not due to nuclear resonance, arising from the
sample, from a comparison between the response signals from
5 the different types of excitation; detecting the response
signals from the sample; and comparing the detected
response signals from the different types of excitation.

This aspect arises from the discovery pursuant to the
10 present invention of certain ways in which the spurious
interfering signals can be distinguished from the genuine
nuclear resonance.

In one preferred embodiment, this distinction can be made
15 by arranging that the different types of excitation are
such as to produce, for the respective response signal from
each different type of excitation, a nuclear response
signal and an interfering signal of a different relative
phase. For example, if the relative phase is 180° (anti-
20 phase), the different types of excitation may be such as to
produce nuclear response signals of different relative
phase.

In another preferred embodiment, this distinction can be
25 made by arranging that the different types of excitation
are such as to produce, for the respective response signal
from each different type of excitation, a nuclear response
signal and an interfering signal of a different relative
amplitude. Preferably, the amplitude of the nuclear
30 response signal differs according to the type of
excitation, whilst the amplitude of the interfering signal
remains the same. For example, the different types of
excitation may be such as to saturate the nuclear response
to different extents.
35

The invention in its various aspects extends to apparatus
equivalent to the above methods. Apparatus features

analogous to the various method features can be provided within the scope of this invention. Further, the various aspects and features of the invention may be combined in any appropriate way.

5

For example, there is provided according to the present invention apparatus for nuclear resonance testing a sample, comprising means for exciting nuclear resonance in the sample using at least two different types of excitation, 10 means for detecting the response signals from the sample, and means for comparing the detected response signals from the different types of excitation.

Preferred features of the invention are now described, by 15 way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a block diagram of apparatus for NQR testing according to the present invention;

Figure 2 is a time-domain plot of a free induction 20 decay (f.i.d.) obtained from a sample comprising the explosive RDX and nickel-plated steel washers;

Figure 3 is a frequency-domain plot corresponding to the time-domain plot of Figure 2;

Figure 4 is a corrected version of the plot of Figure 25 2;

Figure 5 is a frequency-domain plot corresponding to the time-domain plot of Figure 4;

Figure 6 is a plot similar to that of Figure 3 but obtained using a different test;

30 Figure 7 is a corrected version of the plot of Figure 6;

Figure 8 is a plot similar to that of Figure 2, but using a further different test;

Figure 9 is a corresponding frequency-domain plot; and 35 Figure 10 is a corrected version of the plot of Figure 9.

Referring first to Figure 1, apparatus for NQR testing includes a radio-frequency source 11 connected via a phase/amplitude control 10 and a gate 12 to an r.f. power amplifier 13. The output of the latter is connected to an
5 r.f. probe 14 which contains one or more r.f. coils disposed about the sample to be tested (not shown), such that the sample can be irradiated with r.f. pulses at the appropriate frequency or frequencies to excite nuclear quadrupole resonance in the substance under test (for
10 example, an explosive). The r.f. probe 14 is also connected to r.f. receiver and detection circuitry 15 for detecting nuclear quadrupole response signals. The detected signal is sent from circuitry 15 to a computer 16 for processing, for signal addition or subtraction, and
15 thence to an audio or visual alarm 17 which alerts the operator to the presence of the substance under test.

The computer 16 also controls all pulses, their radio frequency, time, width, amplitude and phase; it also checks
20 the tuning of the r.f. probe 14 by means of a pick-up coil 18 and r.f. monitor 19, making adjustments by means of the tuning control 20. The matching to the r.f. power amplifier 13 is monitored by means of a directional coupler 21 (or directional wattmeter), which the computer responds
25 to via a matching circuit 22, which in turn adjusts the r.f. probe 14 by means of a variable capacitance or inductance. The directional coupler 21 is switched out by the computer 16 when not required, via switch 23. The Q factor of the r.f. coil is monitored by a frequency-switch
30 programme and adjusted by means of a Q-switch 24 which either changes the coil Q or alternatively alerts the computer to increase the number of measurements.

The computer 16 may be programmed in various ways to reduce
35 or eliminate the spurious interference described above and caused by materials such as ferromagnetic materials, certain steels and nickel-plated objects.

Not shown in Figure 1 is some means, such as a conveyor belt, for transporting a succession of samples to a region adjacent the r.f. probe 14. The computer 16 is arranged to time the application of the excitation pulses substantially
5 simultaneously with the arrival of a particular sample adjacent the probe.

In a first embodiment of the invention, spurious response signals can be reduced or eliminated by programming the
10 computer to delay the acquisition of data for sufficient time after the end of an r.f. pulse to allow the spurious response signals to decay to insignificance.

In a first variant of this first embodiment, this is
15 achieved by capturing response signals during the f.i.d. excited by an r.f. pulse, after a delay of a predetermined duration following that pulse. This technique is possible when such signals have a decay time which is significantly less than the f.i.d. time of the NQR response.
20
As an example, in Figure 2 the f.i.d. of a sample consisting of 15g of the explosive RDX and 75 g of nickel-plated steel washers at an excitation radio frequency of 5192 kHz and a temperature of 296K is shown. Figure 3
25 shows the corresponding absorption spectrum (that is, the phase-corrected real part of the Fourier transform of the f.i.d.). Figure 2 shows a strong spurious signal at and near the excitation frequency which decays to undetectability in about 500 µs (each division on the
30 horizontal axis represents 500 µs). However, the oscillations from the RDX sample (for which $T_2^* = 1.4$ ms) persist for at least 4 ms; Figure 3 shows a narrow RDX response (the largest peak) superimposed on the broad response of the washers. In Figure 3, the whole range of
35 the horizontal axis represents 25 kHz. Figure 4 shows, to the same horizontal scale as that of Figure 2 but to an enlarged vertical scale, the same f.i.d. but shifted to the

left by 500 µs. Figure 5 shows the corresponding Fourier transform, which reveals only the narrow RDX response, the spurious response having been eliminated.   In the above example, in both the corrected and the uncorrected cases an
5 initial 140 µs was allowed before signal acquisition for probe ring down.

The technique of the first variant can be applied not only to r.f pulses of the optimum "90°" flip angle, but also to
10 those of a different or lower flip angle, and to those which have been amplitude and phase modulated to improve the performance of the NQR test. Because of the loss of some ^{14}N signal during the time delay, however, the signal-to-noise ratio for NQR detection is reduced (the noise
15 remains unchanged, the signal is less). After 500 µs, in the above example the NQR integrated response was reduced by 26%, after 1000 µs by 46%.

Therefore a reduction in signal strength of about 30% would
20 be expected, and, to restore the NQR test to its original sensitivity, an increase in Q factor or number of accumulations by a factor of two will be needed, or possibly a combination of both.

25 In other experiments carried out with nickel plated steel washers and nickel-plated brass nuts it was observed that the duration of the spurious interfering signals at a level greater than noise was 750 µs to 1000 µs, which indicates that a delay of 500-600 µs in addition to the ring down
30 time (say, 600 to 700 µm in total) should be adequate in many circumstances to reduce these spurious signals to acceptable levels. An acceptable level would perhaps be twice, possibly 1.5 or even 1.2 times the average noise level.
35

In other experiments, no spurious interfering signals were detected with pure iron foil, stainless steel or brass. It

is not known for certain what causes such signals in the case of nickel-plated objects.

A second variant of this embodiment is applicable when the
5 echo decay times T_2, T_{2e} are long (for instance, much longer than 1ms) while T_2^* is short. It is applicable to RDX, but is perhaps more useful for substances such as possibly TNT or PETN which have a short T_2^* (for instance, less than 1ms).
10

In this second variant, two or more pulses of selected width and phase are used to generate one or more echoes, for example by the sequence "90°" -τ- "180°" -τ-echo. τ is made shorter than T_2, but, since $T_2 \gg T_2^*$, no signals from
15 interfering materials will usually be detected during acquisition of the echo.

An advantage of this second variant over the first variant is that it is applicable to PETN and TNT, whilst the first
20 variant may not be applicable. However, it has the disadvantage over this first variant of requiring r.f. pulses of sufficient power to produce $90°_{effective}$ ($119°_{actual}$) and $180°_{effective}$ ($259°_{actual}$) flip angles.

25 In a second embodiment of the invention, techniques are employed to distinguish between spurious interfering response signals and the genuine NQR response signals.

A first variant of the second embodiment is particularly
30 appropriate when the f.i.d. time T_2^* is comparable with or shorter than the decay time of the spurious signal. This might be the case with RDX when the interfering material is a piezo-electric material (which exhibits a strong response). In this variant, the spurious signal is
35 eliminated by repeating the test after changing the phase of the NQR response by 180° and then subtracting the two signals. The phase change of 180° may be produced, for

example, by a preliminary "180°" pulse, inserted before the measuring pulse so that two types of pulse sequences are generated, denoted A and B, which give rise to NQR responses of opposite sign (that is, in anti-phase).

5

Pulse sequence A comprises a single measuring pulse, which is a rectangular or amplitude and/or phase-modulated pulse (of "90°", or a different flip angle may be used) following which the f.i.d. is collected and stored. Pulse sequence

10 B is the same, except that it is preceded by a rectangular or amplitude and/or phase-modulated "180°" pulse which inverts the NQR signal. The f.i.d. following the pulse B sequence is then subtracted from that following pulse A, thereby substantially eliminating the spurious response

15 whilst summing the NQR signal.

Figure 6 shows the modulus of the Fourier transformed response from a sample consisting of 15g of RDX and 60g of nickel-plated steel washers; no NQR signal is visible, but

20 it is immediately restored when the two-pulse sequence is used, as shown in Figure 7. Figures 6 and 7 demonstrate that the spurious interfering signal is not phase-shifted, whereas, of course, the NQR response signal is. The frequency range in these two figures is 125 kHz.

25

The two pulse sequences A and B can be generated successively, or an equal number of A pulses can be followed by an equal number of B pulse sequences, and the summed responses then subtracted. Allowance may need to

30 be made for any loss in signal and increase in noise by increasing the Q-factor of the r.f. coil or the number of accumulations.

A second variant of the second embodiment is applicable

35 particularly where the f.i.d. time T_2^* is comparable to or shorter than the decay time of the spurious signal, but where the nature of the sample or the NQR test requires

pulse widths considerably less than "180°" or even "90°" (so that it is not possible to invert the signal). The NQR apparatus is set to generate low flip-angle r.f. pulses, say "30°", by means of rectangular and amplitude and/or 5 phase-modulated pulse waveforms. Pulse sequence A is then a single pulse of this kind following which the full f.i.d., spurious plus NQR response, is collected. Pulse sequence B is then a saturation train of, say, n such pulses of separation τ given by $T_2^* < \tau \ll T_1$, where T_1 is 10 the spin-lattice relaxation time of the NQR response signal; the f.i.d. following the last of those n pulses, consisting of the spurious response only, is then collected and subtracted from the first to give the NQR signal only. It has been found by experiment that n may only need to be 15 2, 3 or 4.

As an example, the resultant f.i.d. for the substance RDX at 5190kHz in the presence of an interfering substance (in this case sand) at 297K is shown in Figure 8. In Figure 8, 20 each division on the horizontal axis represents 200 μs. The pulse sequence (of the "A" type) comprised a "30°" shaped pulse. The resulting f.i.d. after 400 accumulations is shown. Its Fourier transform is shown in Figure 9, in which the total frequency range is 62.5 kHz. Pulse 25 sequence B is a sequence of n=3 such pulses separated by 4 ms ($\tau/T_1 = 0.2$). After 400 accumulations and subtraction of the second signal from the first, the Fourier-transformed response shown in Figure 10 is obtained, in which the spurious signal has been removed, the remaining line being 30 the NQR signal. The frequency range in this figure is 62.5 kHz.

Both variants of the second embodiment have the advantage of not necessarily requiring a delay before signal 35 acquisition, so that no loss of signal occurs, although the noise is increased. However, there are certain conditions when it would be an advantage to combine two or more of the

aforementioned variants, for example when the spurious response is so large that it saturates the amplifier and/or detecting stages. This might occur, for example, in the presence of large quantities of interfering materials, or

5 piezo-electric signals from materials within or close to the r.f. probe. It is then advantageous to introduce a delay before acquisition to reduce the spurious signal to below saturation level, and then remove the remainder by means of one of the variants of the second embodiment.

10

It will be understood that the present invention has been described above purely by way of example, and modifications of detail can be made within the scope of the invention.

15 Each feature disclosed in the description, and (where appropriate) the claims and drawings may be provided independently or in any appropriate combination.

CLAIMS

1.   A method of detecting the presence of a particular substance in a given sample comprising exciting nuclear resonance in the substance and detecting the response signals from the substance, using a probe, and adjusting the probe in dependence on the character of the sample.

2.   A method according to Claim 1 wherein the sample comprises electrically conductive material, for example electronically or ionically conductive material.

3.   A method according to Claim 2 wherein the sample includes metallic material.

4.   A method according to Claim 1, 2 or 3 wherein an electrical characteristic of the probe is adjusted.

5.   A method according to Claim 1, 2, 3 or 4 wherein the impedance of the probe is adjusted.

6.   A method according to any of the preceding claims wherein the tuning of the probe is adjusted.

7.   A method according to any of the preceding claims wherein the Q factor of the probe is adjusted.

8.   A method according to any of the preceding claims wherein the probe is adjusted whilst it is in operation.

9.   A method according to any of the preceding claims wherein interfering signals, not due to nuclear resonance, arising from the sample, are detected, and the probe is adjusted in dependence on the interfering signals.

10.   A method according to Claim 9 wherein the probe is only adjusted if interfering signals are detected.

11. Apparatus for detecting the presence of a particular substance in a given sample, comprising means for exciting nuclear resonance in the substance and for detecting the response signals from the substance, said means including 5 a probe, and means for adjusting the probe in dependence on the character of the sample.

12. Apparatus according to Claim 11, wherein the exciting and detecting means includes means for detecting 10 interfering signals, not due to nuclear resonance, arising from the sample, and the adjusting means is arranged to adjust the probe in dependence on the interfering signals.

13. Apparatus according to Claim 11 or 12 including means 15 for transporting the sample relative to the probe, and wherein the adjusting means is arranged to adjust the probe substantially simultaneously with the arrival of the sample adjacent the probe.

20 14. A method of nuclear resonance testing a sample which gives rise to interfering signals, not due to nuclear resonance, comprising exciting nuclear resonance in the sample, and detecting and processing the response signal from the sample in such a way as to at least partially 25 filter out the interfering signals arising from the sample.

15. A method according to Claim 14, wherein a delay of predetermined duration is provided between the end of the excitation and the beginning of the detection.
30

16. A method of nuclear resonance testing a sample which gives rise to interfering signals, not due to nuclear resonance, comprising exciting nuclear resonance in the sample, and detecting the response signal from the sample, 35 there being a delay of a predetermined duration between the end of the excitation and the beginning of the detection.

17. A method according to Claim 15 or 16 wherein the delay
is sufficient to, preferably only just sufficient to,
substantially filter out interfering signals, not due to
nuclear resonance, arising from the sample.

5

18. A method according to Claim 15, 16 to 17 wherein the
delay is greater than 200 μs, and preferably greater than
400, 500, 600 or even 1000 μs.

10 19. A method according to Claim 15, 16 or 17 wherein the
delay is in the range 200 to 1500 μs, preferably in the
range 400 or 500 to 1000 μs, more preferably in the range
500 to 600 or 700 μs.

15 20. A method according to any of Claims 15 to 19 wherein
the excitation is such as to cause a free induction decay
response signal, and the delay occurs during this response
signal.

20 21. A method according to any of Claims 15 to 20 wherein
the excitation is such as to cause an echo response signal,
and the delay occurs between the end of the excitation and
the echo response signal.

25 22. A method according to any of Claims 15 to 21 wherein
the sample includes metallic material or ferromagnetic
material.

23. A method according to Claim 22 wherein the sample
30 includes metallic or ferromagnetic material as a layer of
plating on another material.

24. A method according to Claim 23 wherein the plating
layer comprises Nickel.

35

25. Apparatus for nuclear resonance testing a sample,
comprising means for exciting nuclear resonance in the

sample, and means for detecting the response signal from the sample, there being a delay of a predetermined duration between the end of the excitation and the beginning of the detection.

5

26. Apparatus according to Claim 25 wherein the delay is greater than 200 µs, and preferably greater than 400, 500, 600 or even 1000 µs.

10 27. Apparatus according to Claim 25 wherein the delay is in the range 200 to 1500 µs, preferably in the range 400 or 500 to 1000 µs, more preferably in the range 500 to 600 or 700 µs.

15 28. A method according to any of Claims 14 to 24, wherein nuclear resonance is excited using at least two different types of excitation, such that the nuclear resonance can be distinguished from interfering signals, not due to nuclear resonance, arising from the sample, from a comparison
20 between the response signals from the different types of excitation, and including the step of comparing the detected response signals from the different types of excitation.

25 29. A method of nuclear resonance testing a sample which gives rise to interference signals, not due to nuclear resonance, comprising exciting nuclear resonance in the sample using at least two different types of excitation, such that the nuclear resonance can be distinguished from
30 the interfering signals, arising from the sample, from a comparison between the response signals from the different types of excitation; detecting the response signals from the sample; and comparing the detected response signals from the different types of excitation.

35

30. A method according to Claim 28 or 29 wherein the different types of excitation are such as to produce, for

the respective response signal from each different type of excitation, a nuclear response signal and an interfering signal of a different relative phase.

5 31. A method according to Claim 28, 29 or 30 wherein the different types of excitation are such as to produce nuclear response signals of different relative phase.

32. A method according to any of Claims 28 to 31 wherein 10 the different types of excitation are such as to produce, for the respective response signal from each different type of excitation, a nuclear response signal and an interfering signal of a different relative amplitude.

15 33. A method according to any of Claims 28 to 32 wherein the different types of excitation are such as to saturate the nuclear responses to different extents.

34. A method according to any of Claims 1 to 10, 14 to 24, 20 or 28 to 33 wherein the sample comprises a nickel-plated object, or piezo-electric material.

35. A method according to any of Claims 1 to 10, 14 to 24, or 28 to 34, wherein the nuclear resonance is nuclear 25 magnetic resonance or nuclear quadrupole resonance, in the latter case preferably in the absence of an applied magnetic field.

36. A method according to any of Claims 14 to 24 or 28 to 30 35, wherein the method is a method of testing for the presence of a sample.

37. A method of testing a sample substantially as herein described.
35

38. Apparatus for testing a sample substantially as herein described with reference to and as illustrated in the accompanying drawings.

5

Amendments to the claims have been filed as follows

1.   A method of detecting the presence in a given sample of a particular substance containing quadrupolar nuclei, 5 comprising exciting nuclear quadrupole resonance in the substance and detecting the response signals from the substance, using a probe, and adjusting the probe in dependence on the character of the sample.

10 2.   A method according to Claim 1 wherein the sample comprises electrically conductive material.

3.   A method according to Claim 2 wherein the sample comprises electronically or ionically conductive material.

15

4.   A method according to Claim 2 or 3 wherein the sample includes metallic material.

5.   A method according to any of the preceding claims 20 wherein the sample comprises a nickel-plated object, or piezo-electric material.

6.   A method according to any of the preceding claims wherein an electrical characteristic of the probe is 25 adjusted.

7.   A method according to any of the preceding claims wherein the impedance of the probe is adjusted.

30 8.   A method according to any of the preceding claims wherein the tuning of the probe is adjusted.

9.   A method according to any of the preceding claims wherein the Q factor of the probe is adjusted.

35

10.   A method according to any of the preceding claims wherein the probe is adjusted whilst it is in operation.

11. A method according to any of the preceding claims wherein interfering signals, not due to nuclear quadrupole resonance, arising from the sample, are detected, and the probe is adjusted in dependence on the interfering signals.

5

12. A method according to Claim 11 wherein the probe is only adjusted if interfering signals are detected.

13. A method according to any of the preceding claims

10 wherein the method is performed in the absence of an applied magnetic field.

14. Apparatus for detecting the presence in a given sample of a particular substance containing quadrupolar nuclei,

15 comprising means for exciting nuclear quadrupole resonance in the substance and for detecting the response signals from the substance, said means including a probe, and means for adjusting the probe in dependence on the character of the sample.

20

15. Apparatus according to Claim 14, wherein the exciting and detecting means includes means for detecting interfering signals, not due to nuclear quadrupole resonance, arising from the sample, and the adjusting means

25 is arranged to adjust the probe in dependence on the interfering signals.

16. Apparatus according to Claim 14 or 15 including means for transporting the sample relative to the probe, and

30 wherein the adjusting means is arranged to adjust the probe substantially simultaneously with the arrival of the sample adjacent the probe.

| Patents Act 1977 | Application number 9419347.1 |
| Examiner's report to the Comptroller under Section 17 (The Search Report) | |

Relevant Technical fields	Search Examiner
	J BETTS
(i) UK Cl (Edition M) G1N (NG32. NG36. NG46)	
(ii) Int Cl (Edition 5) G01N. G01R	

Databases (see over)	Date of Search
(i) UK Patent Office	27 October 1994
(ii) On-line database: WPI	

Documents considered relevant following a search in respect of claims 1-13

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2245364 A (INSTRUMENTARIUM) see pages 10. 12. 13	1-2. 4-5, 8. 11
X	EP 0384061 A (UNIVERSITY OF CALIFORNIA) whole document	1-2. 4. 6. 8. 11
X	EP 0180121 A (GENERAL ELECTRIC) see pages 7-8	1-2. 4. 7-8. 11
X	US 5049821 (UNIVERSITY OF FLORIDA) see column 3	1-2. 8. 11
X	US 4843323 (THOMSON-CGR) see column 1	1-2. 4. 6, 8. 11
X	US 4717881 (TECHNICARE) whole document	1-2, 4. 6, 8. 11
X	US 4587493 (INSTRUMENTARIUM) whole document	1-2. 8. 11
X	US 4602213 (TOKYO) whole document	1-2, 4. 6. 8. 11

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